

ABSTRACT

The development of sustainable technologies applied to the valorization of waste effluents deserves an increasing attention due to the growing demand of the Earth's resources. In this context, electromembrane processes are an emerging alternative for the treatment of metal containing effluents, since they allow the recovery of valuable metals and clean water for reuse, hence implying important benefits for the environment. Industrial effluents that contain multivalent metals can be very diverse and complex, and usually form weak electrolytes. Consequently, the energy consumption and the efficiency of the mass transfer in electromembrane processes are strongly affected by the type of ions that cross the membranes. For this reason, it is important to achieve a better understanding of the mass transfer phenomena involved in these processes in order to make them economically competitive with other less sustainable processes.

Ion sorption properties, chronopotentiometric and current-voltage curves have been obtained in order to characterize the ion uptake equilibrium and the ion transport taking place in systems formed by a Nafion 117 cation-exchange membrane and various metallic solutions. The results obtained with systems of single salt solutions of Na(I), Ni(II), Cr(III) and Fe(III) have proven that the type of species transported through the membranes strongly depends on the initial electrolyte concentration and the applied current density. In systems with trivalent metals, apart from free cations (Cr^{3+} and Fe^{3+}), other charged complex species can cross the membrane (CrSO_4^+ , FeSO_4^+ ...). In systems of multivalent metals and under the application of high current densities, the initial equilibrium conditions at the depleting diffusion boundary layer can be altered, thus inducing the formation of hydroxylated complexes and the formation of precipitates ($\text{Ni}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$) at the depleting membrane surface, which increase the electrical resistance of the membrane systems.

The competitive ion transport through the membranes has been investigated using two different mixtures that resemble the composition of industrial wastewaters. In systems of NiSO_4 and CrO_3 (spent rinse waters of the metal finishing industry), a decrease in the $[\text{Ni}^{2+}]/[\text{H}^+]$ ratio in the equilibrating solution reduced significantly the transport of Ni^{2+} ions through the membranes, but increased the limiting current density and decreased the electrical resistance of the membrane system. In mixtures of $\text{Fe}_2(\text{SO}_4)_3$ and Na_2SO_4 (acid mine drainage), the transport of Na^+ ions occurs preferentially at low current densities and the transport of Fe^{3+} ions at high underlimiting currents. Moreover, the dissociation of FeSO_4^+ ions into Fe^{3+} and SO_4^{2-} ions at high underlimiting currents

promotes a reduction in the electrical resistance of the membrane systems due to the higher conductivity of the free ions with respect to that of complex ionic species.

The overlimiting mechanisms of ion transport have been also investigated. An increase in the concentration of multivalent metals can promote the development of coupled convection (gravitational convection and electroconvection) for lower membrane voltage drops, thus reducing the energy cost of using overlimiting current densities. On the contrary, high concentrations of H^+ ions hamper coupled convection phenomena and increase the membrane voltage drops necessary to reach the overlimiting range of current densities. These results were also corroborated in long-term galvanostatic tests.